



Army Corps
Engineers

AD-A220 495

LONG-TERM EFFECTS OF DREDGING
OPERATIONS PROGRAM

MISCELLANEOUS PAPER D-90-3

SYNOPSIS OF RESEARCH NEEDS WORKSHOP:
DEVELOPMENT OF LEACH TESTS FOR
CONTAMINATED DREDGED MATERIAL

23-24 JUNE 1988, BATON ROUGE, LOUISIANA

by

Louisiana Water Resources Research Institute
Louisiana State University
Baton Rouge, Louisiana 70803

DTIC
ELECTE
MAR 21 1990
S D



February 1990
Final Report

Approved For Public Release; Distribution Unlimited

Prepared for: DEPARTMENT OF THE ARMY
US Army Corps of Engineers
Washington, DC 20314-1000

Under Contract No. DACW39-88-M-1837

Monitored by: Environmental Laboratory
US Army Engineer Waterways Experiment Station
3909 Halls Ferry Road, Vicksburg, Mississippi 39180-6199



21

102

Destroy this report when no longer needed. Do not return
it to the originator

The findings in this report are not to be construed as an official
Department of the Army position unless so designated
by other authorized documents

The contents of this report are not to be used for
advertising, publication, or promotional purposes.
Citation of trade names does not constitute an
official endorsement or approval of the use of
such commercial products.

The D-series of reports includes publications of the
Environmental Effects of Dredging Programs:
Dredging Operations Technical Support
Long-Term Effects of Dredging Operations
Interagency Field Verification of Methodologies for
Evaluating Dredged Material Disposal Alternatives
(Field Verification Program)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) Miscellaneous Paper D-90-3		
6a. NAME OF PERFORMING ORGANIZATION Louisiana Water Resources Research Institute		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION USAEWES Environmental Laboratory		
6c. ADDRESS (City, State, and ZIP Code) Louisiana State University Baton Rouge, LA 70803			7b. ADDRESS (City, State, and ZIP Code) 3909 Halls Ferry Road Vicksburg, MS 39180-6199		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION US Army Corps of Engineers		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. DACW39-88-M-1837		
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20314-1000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Synopsis of Research Needs Workshop; Development of Leach Tests for Contaminated Dredged Material, 23-24 June 1988, Baton Rouge, Louisiana					
12. PERSONAL AUTHOR(S)					
13a. TYPE OF REPORT Final report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) February 1990	
				15. PAGE COUNT 34	
16. SUPPLEMENTARY NOTATION Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	→ Confined disposal Dredged material		
			Contaminant mobility Leach tests		
			Contaminated sediment		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) — This report presents the findings of a research needs workshop on the development of leach tests for contaminated dredged material, held 23-24 June 1988 in Baton Rouge, LA. The workshop was hosted by the Louisiana Water Resources Research Institute and the US Army Engineer Waterways Experiment Station (WES). The workshop participants reviewed results of research on test procedures developed by the WES and provided eight recommendations for directing future research in this area. Workshop panelists were of the opinion that research conducted to date was good and generally validated the basic technical approaches suggested by the 1984 Corps leachate quality working group. However, the consensus was that much research remains to be done before a leach test(s) will be available for routine use.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

PREFACE

A research needs workshop on the development of leach tests for contaminated dredged material was held 23-24 June 1988 in Baton Rouge, LA. The workshop was hosted by the Louisiana Water Resources Research Institute (LWRRI), the Hazardous Waste Research Center (HWRC), and The Center for Wetland Resources (CWR), all of Louisiana State University (LSU), Baton Rouge.

Funding was provided by the Long-Term Effects of Dredging Operations (LEDO) research program of the US Army Corps of Engineers (USACE). Technical monitors for LEDO are Dr. Robert J. Pierce, Dr. William L. Klesch, and Mr. David B. Mathis of the Headquarters, USACE. The LEDO Program is managed by the Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES), as part of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, Manager. The LEDO Program Coordinator was Mr. Russell F. Theriot.

Workshop participants included Dr. James M. Brannon and Mr. Tommy E. Myers, WES; Dr. Marty Tittlebaum and Ms. Brenda Kelly, LWRRI-LSU; Dr. Louis Thibodeaux, HWRC-LSU; Dr. Robert Gambrell and Dr. William Patrick, CWR-LSU; Dr. Steve McCutcheon, Environmental Research Laboratory, US Environmental Protection Agency, Athens, GA; Dr. Cass Miller, University of North Carolina, Chapel Hill, NC; Dr. Thomas Murphy, DePaul University, Chicago, IL; and Dr. Paul Roberts, Stanford University, Stanford, CA.

This report was prepared by the LWRRI-LSU for the WES under Contract No. DACW39-88-M-1837. The WES contract monitor was Mr. Myers. The report was prepared for publication by Ms. Jessica S. Ruff of the WES Information Technology Laboratory.

The work was conducted under the direct supervision of Mr. Norman R. Francingues, Jr., Chief, Water Supply and Waste Treatment Group, Environmental Engineering Division (EED), and Dr. Thomas L. Hart, Chief, Aquatic Processes and Effects Group, Ecosystem Research and Simulation Division (ERSD), and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, Mr. Donald L. Robey, Chief, ERSD, and Dr. John Harrison, Chief, EL.

Commander and Director of WES at the time of publication was COL Larry B. Fulton, EN. Technical Director was Dr. Robert W. Whalin.

This report should be cited as follows:

Louisiana Water Resources Research Institute. 1990. "Synopsis of Research Needs Workshop: Development of Leach Tests for Contaminated Dredged Material, 23-24 June 1988, Baton Rouge, Louisiana," Miscellaneous Paper D-90-3, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

CONTENTS

	<u>Page</u>
PREFACE.....	1
PART I: INTRODUCTION.....	4
Background.....	4
Scope.....	5
PART II: TECHNICAL HIGHLIGHTS OF WORKSHOP.....	6
Site and Dredged Material Characteristics.....	6
Tiered Approach.....	6
Colloidal Systems.....	7
Factors Affecting Batch Test Results.....	7
Equilibrium in Batch Tests.....	8
Modifications to Column Leach Test.....	8
Chemical Techniques for Accelerated Sediment Oxidation.....	9
Mass Transport Modeling.....	10
Verification.....	10
PART III: DIRECTIONS FOR FUTURE RESEARCH.....	12
REFERENCES.....	13
APPENDIX A: DISCUSSION PAPER ON DEVELOPMENT OF LEACH TESTS FOR CONTAMINATED DREDGED MATERIAL.....	A1
APPENDIX B: SUMMARY OF RESEARCH METHODOLOGIES.....	B1

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

SYNOPSIS OF RESEARCH NEEDS WORKSHOP: DEVELOPMENT OF LEACH
TESTS FOR CONTAMINATED DREDGED MATERIAL
23-24 JUNE 1988, BATON ROUGE, LOUISIANA

PART I: INTRODUCTION

Background

1. The US Army Corps of Engineers has responsibility for maintaining 40,000 km of navigable waterways. In maintenance of these waterways, the Corps dredges approximately 290 million cubic metres of sediment annually. Disposal of this enormous volume of dredged material is a major effort, especially for the approximately 3 percent that is unsuitable for unrestricted management.

2. The potential presence of contaminants in sediments has generated concern that relocation of dredged material may adversely affect water quality and aquatic, wetland, or terrestrial organisms. These concerns have led to the regulation of dredged material disposal under Section 404 of the Clean Water Act and Section 103 of the Marine Protection, Research and Sanctuaries Act. These regulations result in restrictions on management for some projects and often delay dredging activities.

3. Relocation of approximately 3 percent of the materials dredged yearly is restricted. When the potential for adverse environmental impacts exists, upland site management operations must be carefully planned to restrict contaminant movement from the site into surrounding soils and/or surface and ground water.

4. Dredged materials considered unsuitable for open-water sites must be confined in some manner. Design of a confined disposal facility (CDF) requires information on the quality of leachate generated by the relocated dredged material. This information is needed prior to dredging operations in order to evaluate the confined upland alternative. Lacking specific quantitative information on leachate quality, project engineers are forced to adopt contaminant containment strategies that are possibly more conservative and costly than necessary.

5. At present, there is no routinely applied laboratory testing protocol capable of predicting leachate quality in confined dredged material upland sites. Therefore, testing procedures to predict leachate quality are needed to fully evaluate the confined upland alternative for dredged material. If leachate quality and quantity can be predicted, the potential impacts of management of contaminated dredged material in a CDF can be determined, thus allowing the most cost-effective and environmentally sound containment strategy to be used.

6. Experimental procedures for predicting leachate quality have been used to evaluate the potential impacts of confined upland management of dredged material from Indiana Harbor, Indiana, Everett Harbor, Washington, and New Bedford Harbor, Massachusetts (Environmental Laboratory 1987; Myers and Brannon, in preparation; Palermo et al., in preparation). A brief discussion paper (Appendix A), summarizing the results of these leaching studies, was prepared for the workshop participants to review. Procedures used to obtain the results presented in Appendix A are summarized in Appendix B. These procedures were based on relevant knowledge and recommendations gathered during a 1984 workshop on the development of leach tests for dredged material (Hill, Myers, and Brannon 1988).

Scope

7. This report presents a synopsis of the relevant knowledge and recommendations gathered at a research needs workshop on the development of leach tests for contaminated dredged material, 23-24 June 1988, in Baton Rouge, LA. The workshop was organized to assemble prominent researchers in the area of contaminant mobility in dredged material. The participants reviewed results of research on test procedures developed since the workshop in 1984 (Hill, Myers, and Brannon 1987) and provided recommendations for future research in this area. Recommendations were developed during workshop discussions of past leach testing, with emphasis on current problems and future research needs.

PART II: TECHNICAL HIGHLIGHTS OF WORKSHOP

8. This section summarizes the discussion session of the workshop. Workshop panelists were of the opinion that work conducted to date was good and generally validated the basic approaches suggested by the 1984 working group. However, the consensus was that much research remains to be done before a leachate test(s) will be ready for routine use. Highlights presented in this section are not ranked in order of priority, since identification of priorities was not an objective of the workshop.

Site and Dredged Material Characteristics

9. A major technical highlight identified during the workshop was the importance of considering how the properties of dredged material and the short- and long-term physical and chemical environment of the dredged material in a confined site influence contaminant mobility. Leach tests should be capable of simulating contaminant leaching for the physical, chemical, biological, and engineering characteristics of the dredged material and the disposal site. These characteristics can greatly impact both leachate quality and the type of testing needed. For example, leaching conditions for dredged material placed in an upland site would differ considerably from those needed for an in-water estuarine site. Site-specific test procedures are expected to provide the most reliable information on quality of both short- and long-term leachates.

Tiered Approach

10. A tiered approach was agreed upon by the workshop participants as a logical and cost-effective method for implementation of the suite of tests that may be needed to determine the leaching potential of different contaminants and types of dredged material under various confined site conditions. The tiered approach begins with simple and inexpensive procedures and moves to more complex methods, some requiring substantial resources, as the detail and reliability of the information needed increase. A tiered approach consisting of three major levels was discussed. The first tier involves application of simple transport models using bulk chemistry and physical property data to

predict leachate quality. The second tier involves application of screening-level leach tests to indicate potential leachate quality and/or to provide input to more complicated transport models. The third tier involves application of state-of-the-art laboratory leach tests and appropriate transport models.

Colloidal Systems

11. Discussion was held concerning the apparent microparticle-mediated transport of polychlorinated biphenyls (PCBs) into batch test leachate during testing of sediment from the New Bedford Harbor Superfund Site, New Bedford, MA. Workshop participants agreed that destabilization of the colloidal system was probably responsible for increasing PCB concentrations in New Bedford Harbor sequential batch leachate. Mobilization of colloidal matter and microparticles and the mode of contaminant association with these phases were identified as areas of needed study. Possible approaches to investigating colloid and microparticle mobilization include using particulate fractionation by filtration and centrifugation, fugacity determinations based upon measurement of organic contaminant concentrations in air in equilibrium with organic contaminant concentrations in leachate and sediment, and the use of recirculating thin column reactors.

Factors Affecting Batch Test Results

12. Extended discussions were held concerning factors affecting batch tests in the testing of Indiana Harbor, Everett Harbor, and New Bedford Harbor sediments. Discussion centered on changes in environmental conditions, such as ionic strength and pH, that occurred during sequential leaching and the impact these changes have on contaminant partitioning. The problem of multiple phases (wide array of contaminants, oil, organic matter, sediment solids) in the sediment-water system was discussed. Particular emphasis was placed on the complexity that multiple phases add to any test procedure. It was agreed, based upon discussions of results, that batch test leaching conditions should be adjusted according to the site characteristics being simulated (e.g., saline water, fresh water, upland site, or in-water CDF). These changes would result in different factors of concern during testing. For example, leaching

of saline sediment with fresh water may result in mobilization of dissolved organic carbon (DOC) and associated contaminants as the ionic strength of the leachate decreases and destabilization of colloidal matter and flocculated aggregates occurs. One way to examine the impact of factors affecting leachate quality is to conduct a complete chemical characterization of the leachate for major cations and anions, and to more completely characterize sediment geochemistry.

13. The effects of shear stresses on sediment particles and solids concentration during batch testing were also discussed. The effect that breaking of particle aggregates into smaller units has on contaminant releases and the implications this has for column test results were discussed. Procedures that employ gentle shaking as well as thin-column recirculation tests were discussed as means of investigating the differing physical conditions inherent in batch and column testing.

Equilibrium in Batch Tests

14. Kinetic batch test results showed that "steady-state" leachate concentrations for PCBs were reached during the 24-hr tests. Discussion centered on rapid and slow desorption of PCBs from sediment particles and how to determine if equilibrium had been reached in the leachate. Kinetic testing to characterize the leachate time-concentration curve prior to and beyond 24 hr was discussed as an approach for evaluating equilibrium. Another means of determining the status of equilibrium is the use of a thin-layer column with leachate recirculation. In this way, both kinetics and equilibrium can be tested and evaluated.

Modifications to Column Leach Test

15. Participants agreed that, in theory, column leach tests provide better simulation of field processes than batch leach tests. However, several problems with the column leach test were identified, and suggestions were made for improvement. The major problem areas discussed were as follows: slow percolation rates, possible compositional changes in leachate during sample collection, and shifts from aerobic to anaerobic conditions during aerobic column leach tests. Each of these problem areas is briefly discussed below.

Percolation rates

16. Discussion of percolation rates centered around the advantages of a short, large-diameter column (thin-layer column). A thin-layer column design should alleviate some of the operational problems experienced with the present column design. The time required to collect a sample and run a column leach test would be significantly shortened, dead zones and wall effects would be minimized, and recirculation, a technique for determining equilibrium concentrations, would be possible.

Sampling strategy

17. Several participants expressed concern about sample integrity during column leach testing. Holding time in the leachate collection vessel (approximately 30 days) was considered too long. This problem could be reduced, but not eliminated, by column redesign, as discussed previously. Maintaining sample integrity for metals may require the monitoring and adjustment of pH. For hydrophobic organics, continuous extraction of leachate during collection may be necessary.

Aerobic column tests

18. Several participants suggested that aerobic column tests should be reexamined. Inability to maintain oxidized conditions for preoxidized sediment during "aerobic" column leaching precludes simulation of aerobic leaching conditions. The aerobic column leach tests apparently simulate flooded, partially oxidized dredged material, such as may exist in CDFs during rainfall events. The significance of leaching under these conditions should be established, or the test should be modified or abandoned.

Chemical Techniques for Accelerated Sediment Oxidation

19. The length of time required to oxidize dredged material for testing (6 months) and the rapid return of the "oxidized" dredged material to anaerobic conditions when air was excluded during column testing were discussed. The time needed to partially oxidize the dredged material was considered excessive, especially if answers to aerobic leachate questions are required in a short time frame. Discussion centered on possible screening-level tests to chemically oxidize the sediment and to determine if a pH drop resulting in metal mobilization would occur upon exposure to air. The effects of chemical

oxidation on sequential batch leach test results, and possibly on column testing, should also be evaluated.

Mass Transport Modeling

20. Workshop participants viewed modeling of the interphase transfer of contaminants from dredged material solids to water as something that is technically very difficult, although required for development and verification of simplified leach tests for routine application to dredged material. Several factors that complicate modeling efforts and that are specific to dredged material were noted. Dredged material solids may contain many contaminants, e.g., metals and organics, that do not desorb independently. Further, the colloidal system is probably a controlling factor in leaching of many contaminants, especially organics. Also, contaminants have usually been in contact with the solids for many years, allowing time for migration into sediment intraparticle pores where they are relatively immobile. Sorption models that do not account for the colloidal system, intraparticle pore phenomena, and multicomponent effects may be inadequate.

21. Mass transport modeling will probably require mass balances on at least three phases--solids, water, and colloidal material. Although modeling should focus on contaminants of principal concern, concurrent modeling of other parameters such as DOC, ionic strength, and secondary reactions that affect release may be necessary. A series of mass balances will be required. Conceptually, the modeling effort is feasible. However, the workshop participants cautioned that significant time and effort will be required.

Verification

22. An important technical need identified by the workshop participants was verification of the test procedures developed for contaminated dredged material. Verification will establish the predictive capability of tests under field conditions and determine if modification is needed.

23. Three suggestions for implementing verification were proposed at the workshop. One was to use existing confined facilities with identifiable leaching characteristics for collection of verification data. Another was to

use large-scale models that will physically simulate the leaching conditions of various confinement options. A third option was to develop a multiagency national study site specifically selected for contaminated dredged material leaching research and development activities. Such a site would be a cost-effective method of providing the experimental controls needed to verify leaching procedures under field conditions.

PART III: DIRECTIONS FOR FUTURE RESEARCH

24. The following directions for future research were identified during the workshop. Recommendations were as follows:

- a. Redesign the column leach test to include thin-layer columns and improved leachate collection systems.
- b. Reevaluate the aerobic column test.
- c. Investigate the impact of colloidal systems on interactions between solid and liquid phases.
- d. Determine the role of key parameters such as ionic strength, pH, and contaminant-sediment association on leachate results.
- e. Investigate desorption kinetics.
- f. Investigate techniques for accelerated sediment oxidation.
- g. Develop a more comprehensive model and verify the model structure for comparing batch and column test results.
- h. Verify test protocols in a field situation, preferably at a multiagency national research site.

REFERENCES

Environmental Laboratory. 1987. "Disposal Alternatives for PCB-Contaminated Sediments from Indiana Harbor, Indiana; Vol II: Appendixes A-J," Miscellaneous Paper EL-87-9, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Hill, D. O., Myers, T. E., and Brannon, J. M. 1988. "Development and Application of Techniques for Predicting Leachate Quality in Confined Disposal Facilities: Background and Theory," Miscellaneous Paper D-88-1, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Myers, T. E., and Brannon, J. M. "New Bedford Harbor Superfund Project, Acushnet River Estuary Engineering Feasibility Study of Dredging and Dredged Material Disposal Alternatives; Report 5, Evaluation of Leachate Quality," Technical Report EL-88-15, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Palermo, M. R., Shafer, R. A., Brannon, J. M., Truitt, C. L., Zappi, M. E., Skogerboe, J. G., Adamec, S. A., Sturgis, T. C., Wade, R., Gunnison, D., and Myers, T. E. "Evaluation of Dredged Material Disposal Alternatives for US Navy Homeport at Everett, Washington," Technical Report (in preparation), US Army Engineer Waterways Experiment Station, Vicksburg, MS.

APPENDIX A: DISCUSSION PAPER ON DEVELOPMENT OF LEACH TESTS FOR CONTAMINATED DREDGED MATERIAL

Introduction

1. When contaminated dredged material is placed in an upland or near-shore confined site, the potential exists to generate leachates that may adversely impact surface and ground waters. Currently, there are no standard laboratory tests capable of predicting leachate quality from confined dredged material sites. Experimental procedures for predicting leachate quality are being used on a case-by-case basis to evaluate the potential impacts of managing dredged materials in confined sites. These leaching procedures are in an early stage of development but have been used in studies at Indiana Harbor, Indiana, Everett Harbor, Washington, and New Bedford Harbor, Massachusetts (Environmental Laboratory 1987; Myers and Brannon, in preparation; Palermo et al., in preparation*). During the course of these studies, kinetic, sediment-water ratio, and sequential batch tests have been conducted in conjunction with permeameter testing.

2. This discussion paper summarizes test results obtained to date at the US Army Engineer Waterways Experiment Station with regard to contaminant leaching from dredged material. It also includes a section on general research approaches under consideration for development of a leachate testing protocol.

Leachate Test Results

Indiana Harbor

3. Operational difficulties incurred during the batch testing of Indiana Harbor sediment were pronounced because of the oil and grease content (3.88 percent) of the sediment. During batch testing, the oil emulsified and could be separated from the water only by extensive centrifugation. More oil was released during batch tests with lower sediment-to-water ratios. Several centrifugation steps were required to break the emulsion. For example, nine centrifugations were required to completely remove oil from the anaerobic

* See References at the end of the main text.

interstitial water sample for organic analysis. Oil removal was necessary because the oil was highly contaminated with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons, and would bias the results of the batch testing.

4. In general, anaerobic sequential batch tests for metals produced well-defined desorption isotherms, and aerobic sequential batch tests for metals produced ill-defined clusters. An example is presented in Figure A1 for zinc and cadmium. Batch aerobic desorption data for all metals tested were clustered and did not exhibit well-defined isotherms (Figure A1).

5. The PCB desorption isotherms were characterized by clustering of data, indicating that PCBs were tightly bound to the sediment solids (high K_d) or, alternatively, that the distribution coefficient varied during the sequential leaching procedure, or both. Because of the clustering, single-point distribution coefficients were calculated.

6. Continuous-flow column leaching tests were conducted in divided-flow permeameters (Figure A2) using both anaerobic and aerobic Indiana Harbor sediment. The data generally indicated that as the number of pore volumes of water passed through the sediment increased, the contaminant concentrations in the leachate decreased.

7. The integrated approach, outlined in Figure A3, was applied to the Indiana Harbor batch and permeameter data. An application for total PCB congeners is illustrated in Figure A4. Predicted concentrations were plotted for two conditions. The first assumes that contaminant leaching in the permeameters is governed by equilibrium-controlled, linear desorption and that the equilibrium distribution coefficient is adequately described by the K_d obtained using sequential batch leach tests. The second condition assumes that desorption does not occur; that is, K_d is equal to zero. The data, presented in Figure A4, showed that there was some PCB desorption, but not as much as predicted. Overall, prediction of PCB elution was within an order of magnitude of the observed elution and was conservative; that is, predicted concentrations were generally higher than observed concentrations.

8. The major conclusions from the Indiana Harbor studies were as follows:

- a. Assumption of equilibrium-controlled, linear desorption for the source term in a permeant-porous media equation for PCBs conservatively predicted leachate contaminant concentrations.

- b. Less than 1 percent of the bulk metal concentration in Indiana Harbor sediment was leachable.

Everett Harbor

9. Results from Everett Harbor sediment leach testing differed sharply from the Indiana Harbor results. Contaminant concentrations were much lower, especially for organic contaminants, and the sediment was from a brackish environment rather than a freshwater environment. Concentrations of organic contaminants in the sediment were too low to merit discussion. This sediment developed a low pH when allowed to oxidize, resulting in mobilization of metals from aerobic sediment during sequential batch leaching.

10. Desorption isotherms for arsenic and copper obtained during anaerobic sequential batch leaching are illustrated in Figures A5 and A6, respectively. Release of metals from anaerobic sediment did not follow the classical desorption observed for metals in anaerobic Indiana Harbor sediment. The arsenic desorption isotherm showed a reverse slope that transitioned to a relatively well-defined desorption isotherm following peak concentrations. The copper desorption isotherm showed a reverse slope throughout sequential leaching. The turning point for the arsenic desorption isotherm was coincident with establishment of steady leachate pH.

11. Leachate pH in aerobic Everett Harbor sediment was 4.3, resulting in mobilization of some metals during sequential batch leaching. Desorption isotherms for most metals displayed the reverse slope observed for anaerobic copper (Figure A6).

12. Because the contaminant transport equation requires constant values of K_d , it was not possible to predict permeameter leachate concentrations using the integrated approach applied to the Indiana Harbor batch and permeameter data. A simplified method that related pore volumes in the sequential batch tests to pore volumes in the permeameter tests was therefore used. In the region where observed and predicted results could be compared ($1.1 < \text{pore volume} < 3.0$), qualitative agreement was good for some metals but not for others.

13. Batch desorption coefficients determined under aerobic conditions could not be used to predict contaminant concentrations from permeameters initially filled with aerobic sediment. Even sediment placed in an oxidizing environment for 6 months retained sufficient oxygen demand to become anaerobic once it was placed in a column and flooded.

14. Results of follow-on testing of Everett Harbor sediment indicate that the type of leaching solution (saline versus freshwater) and the final filtration step (0.1- or 0.45- μ m membrane filters) can strongly influence metal sequential leachate results.

New Bedford Harbor

15. The New Bedford site differed from previous sediment tested in that it contained 2,167 mg/kg of total PCB, orders of magnitude higher in concentration than observed for Indiana Harbor and Everett Harbor sediment. Many metals in New Bedford sediment were also higher than 1,000 mg/kg in concentration.

16. As illustrated in Figure A7 for nickel, desorption isotherms with reverse slopes were obtained for metals from sequential batch leaching of anaerobic New Bedford sediment. Aerobic New Bedford sediment developed a low pH during leaching (low of 2.1). Metal releases were therefore high and developed reverse desorption isotherms similar to, though steeper in slope than, the isotherm presented for anaerobic nickel leaching (Figure A7).

17. Leaching of anaerobic New Bedford sediment with distilled water resulted in nonconstant partitioning with development of reverse slope isotherms that in some cases turned back toward the sorbed concentration (vertical) axis. This is illustrated in Figure A8 for total PCB. Leaching of New Bedford sediment with saline (20 ppt) water demonstrated partitioning behavior generally consistent with classical theory. This is illustrated in Figure A9 for total PCB.

18. Leaching of anaerobic New Bedford sediment with distilled water resulted in mobilization of PCBs, whereas leaching with saline water resulted in relatively lower mobilization (Figure A10). The trends observed in PCB concentrations between distilled and saline water leachate (Figure A10) were similar to the trends observed for levels of microorganisms (Figure A11) and dissolved organic carbon (DOC) in the leachate (Figure A12). These data suggest that, as conductivity in the distilled water leachate decreased, colloidal organic matter and microorganisms containing adsorbed PCB were destabilized, resulting in PCB mobilization in colloidal or microparticulate form.

19. Significantly lower concentrations of PCBs and some metals were observed in permeameter leachate compared with batch leachate. The reasons for these significant differences are presently unexplained.

20. As was the case with Everett Harbor, the integrated approach could not be used with New Bedford sediment because of nonconstant partitioning during batch testing. It was possible, however, to simulate PCB elution during nonconstant partitioning by coupling PCB concentrations to conductivity in permeameter leachate. Predicted and observed curves were in relatively good agreement for PCB. This approach could not be applied to anaerobic metals, because some metals did not show peak concentrations in the leachate, and nonconstant partitioning of metals was not demonstrated to be related to conductivity changes.

Contemplated Future Work

21. In the leachate studies conducted to date, each of the sediments tested behaved in a unique manner. Future study will build on the lessons learned in these projects, focusing on development, simplification, and verification of a leachate testing protocol for dredged material.

22. The studies conducted to date have shown that contaminant release trends predicted by batch and permeameter testing generally show qualitative agreement, and for Indiana Harbor, the agreement was quantitatively good. However, the studies suggest the need for a thorough investigation of the factors affecting leachate quality in batch and permeameter testing. For some sediments, the permeameter data were orders of magnitude lower than batch testing data, even though release trends agreed qualitatively. The batch and permeameter test procedures need to be investigated to determine why the data do not agree more closely. Factors potentially affecting batch and permeameter leachate results include the effects of pore water velocity and shear, possible adsorption by collection vessels and tubing, underestimation of permeameter distribution coefficients by batch test procedures, and nonequilibrium desorption in the permeameters. In addition, the factors that result in nonconstant partitioning in the batch tests need to be investigated further, especially for metals. The work conducted to date has identified conductivity washout, pH changes, filter pore size, and changes in the nature of DOC releases as possible factors resulting in nonconstant partitioning during batch testing.

23. Research on permeameter testing is needed in several areas. The potential for sorption losses in the collection vessels during testing should

be examined. Improved sample collection and preparation techniques may be required. The effects of sediment preparation prior to permeameter loading upon particle aggregation and potential contaminant leaching need to be investigated. Consolidation and the effects of consolidation on flow-related variables need to be accounted for. Biodegradation is another process currently unaccounted for in permeameter testing. The Everett Harbor and New Bedford Harbor studies indicated that numerous multicomponent sediment-water interactions are involved in leaching that cannot be modeled with a single set of desorption coefficients. Application of the integrated approach will probably require development of a mathematical model capable of using all the information provided by the batch test.

24. Key decisions will have to be made on which factors to control during batch and permeameter leaching and which to allow to proceed. Results to date have shown that changes in pH, conductivity, and DOC observed during batch testing are mirrored in permeameter testing. Follow-on testing has also shown that aging of sediment can affect the amount of metals and PCBs released. It is not reasonable to expect that sediment geochemistry will remain constant indefinitely. The effort to date has addressed this problem by examining leachate from anaerobic and aerobic sediment. Changes in sediment geochemistry during leach testing need to be investigated directly.

25. Later steps in the research program will involve verification of laboratory leaching tests and development of simplified test procedures and mass transport equations applicable to various situations. In the three sediments studied to date, different ways of comparing batch and permeameter test results have been required for each sediment. This approach is not an option for the final predictive test, which must have general applicability.

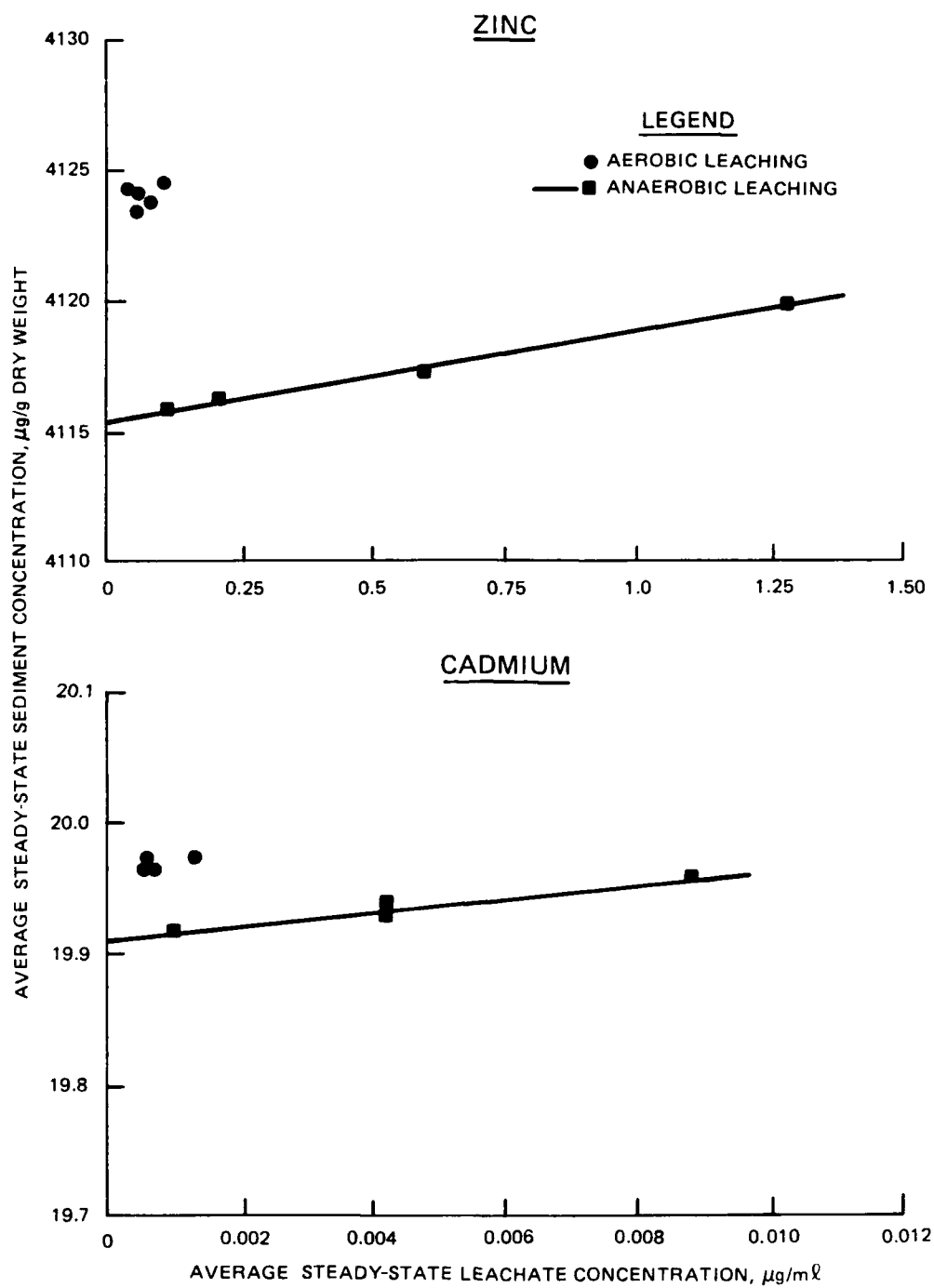


Figure A1. Desorption isotherms for zinc and cadmium in Indiana Harbor sediment

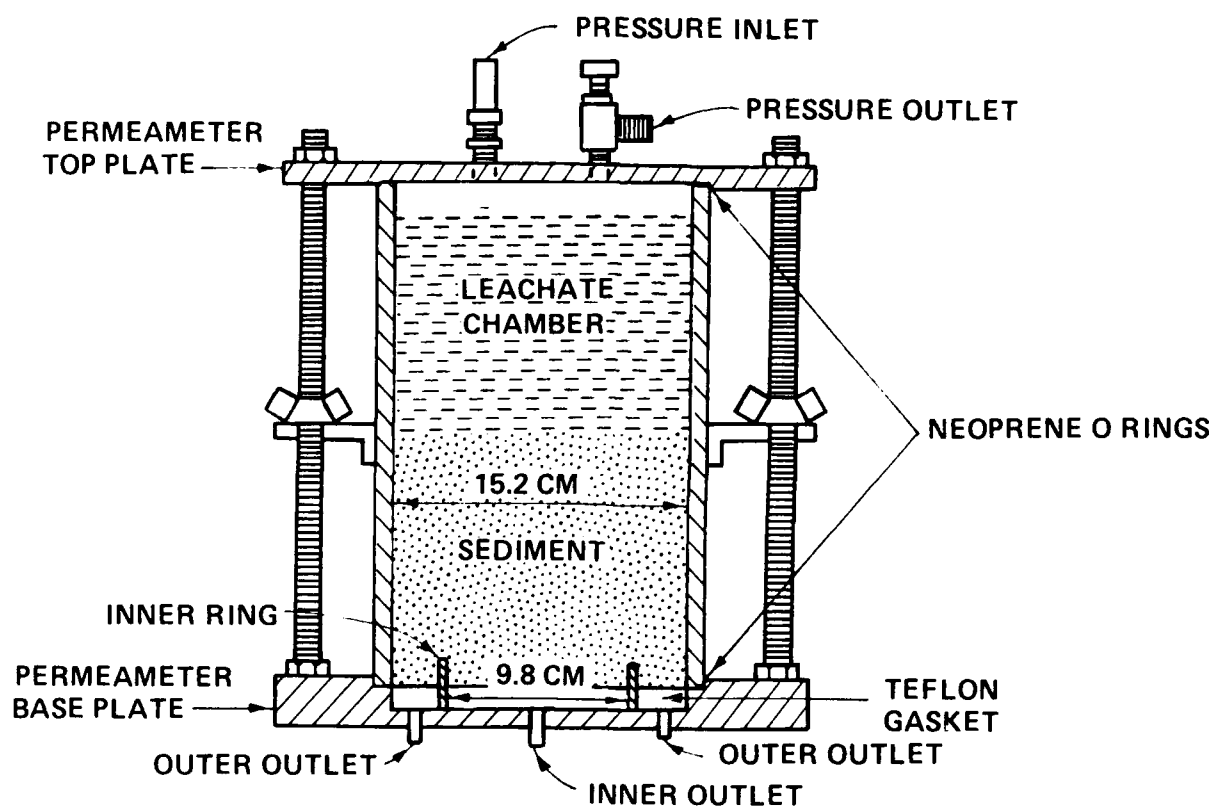


Figure A2. Divided-flow permeameter

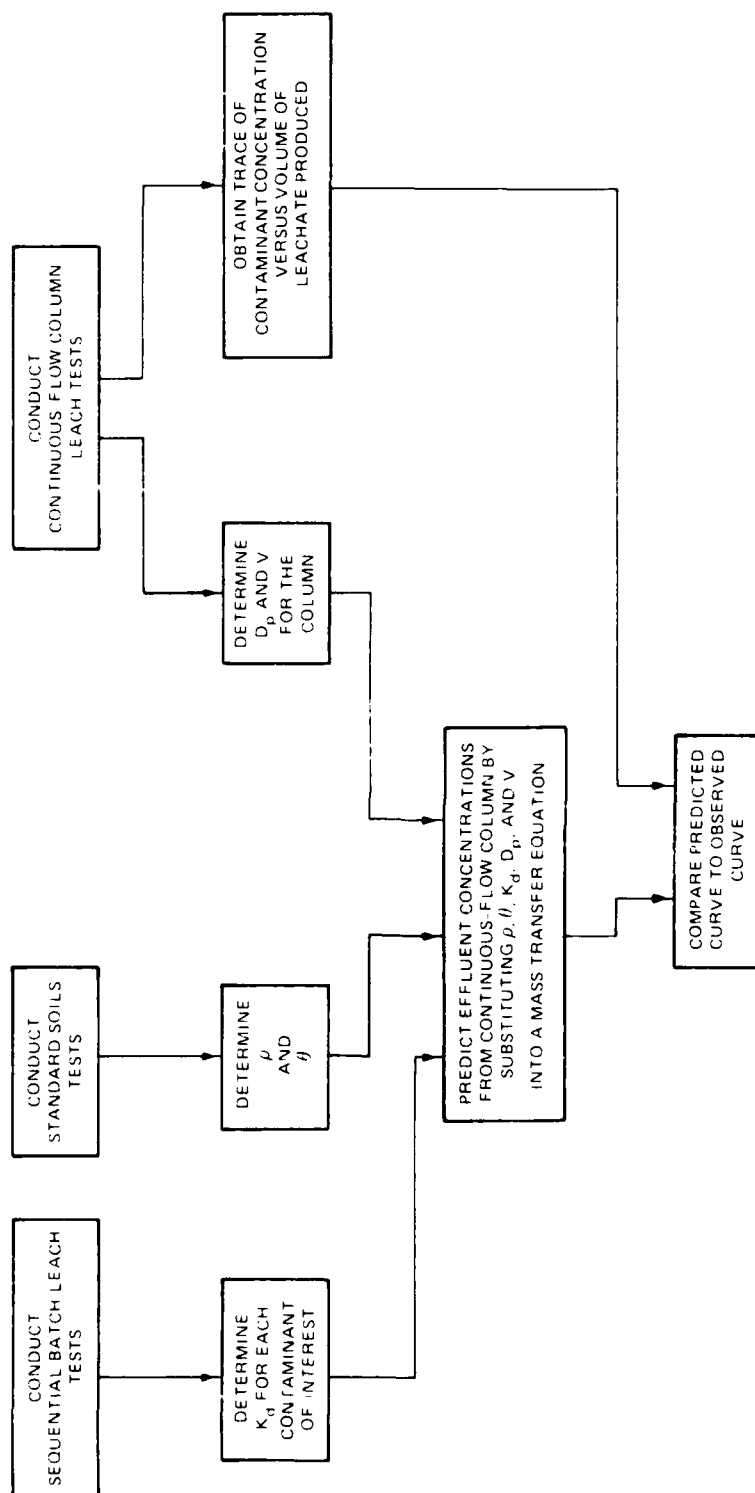


Figure A3. Schematic of integrated approach for examining the source term

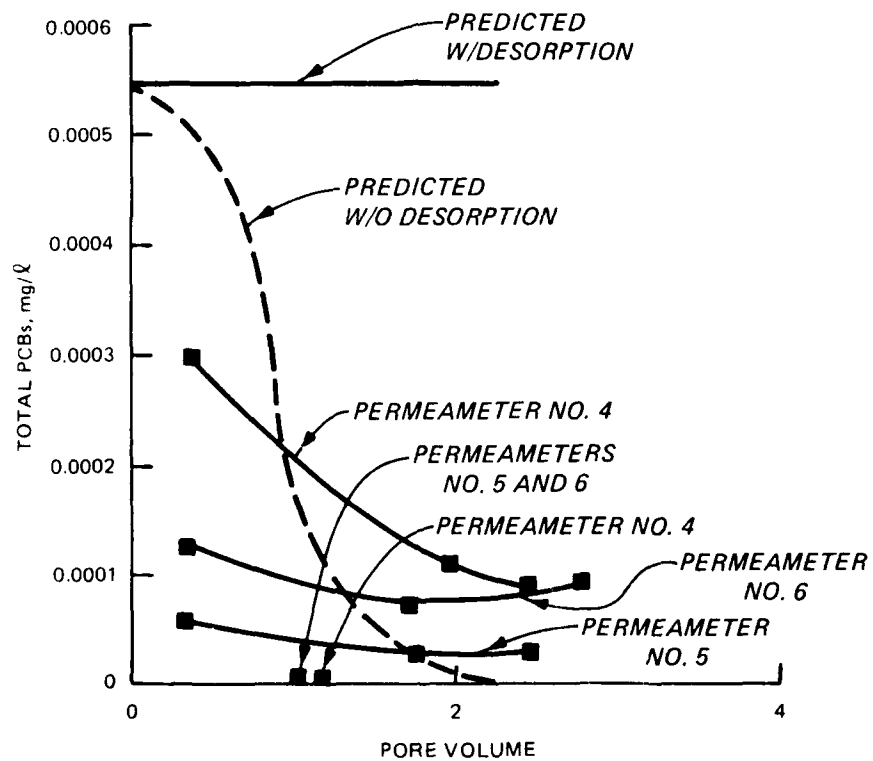


Figure A4. Total PCB concentration in anaerobic permeameter leachate

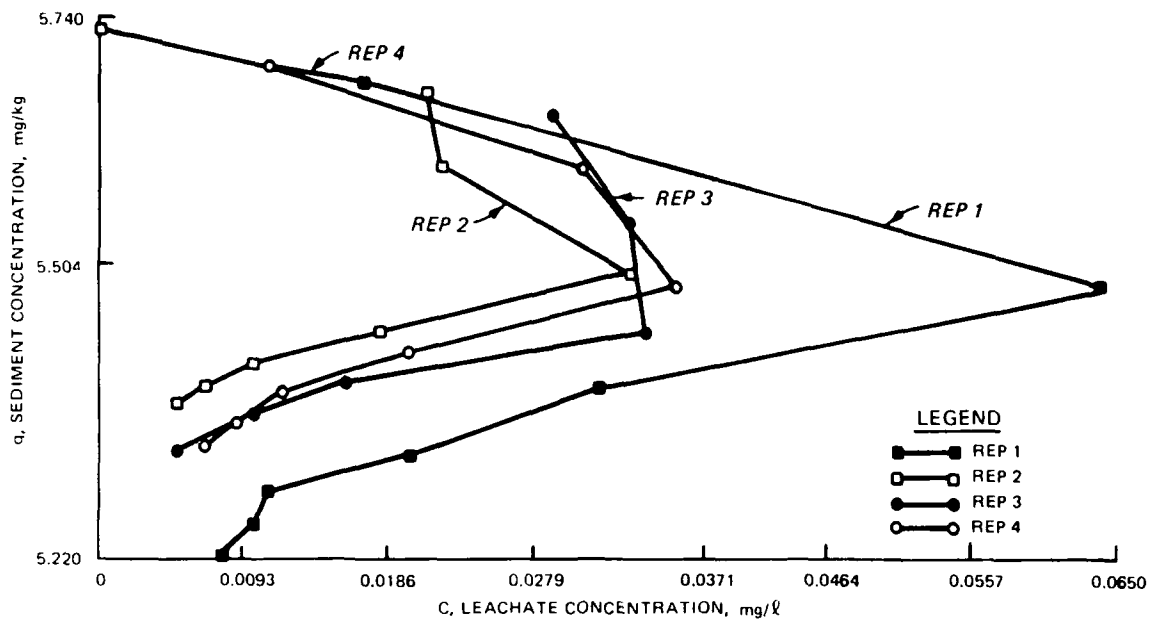


Figure A5. Arsenic desorption isotherm for anaerobic Everett Harbor sediment

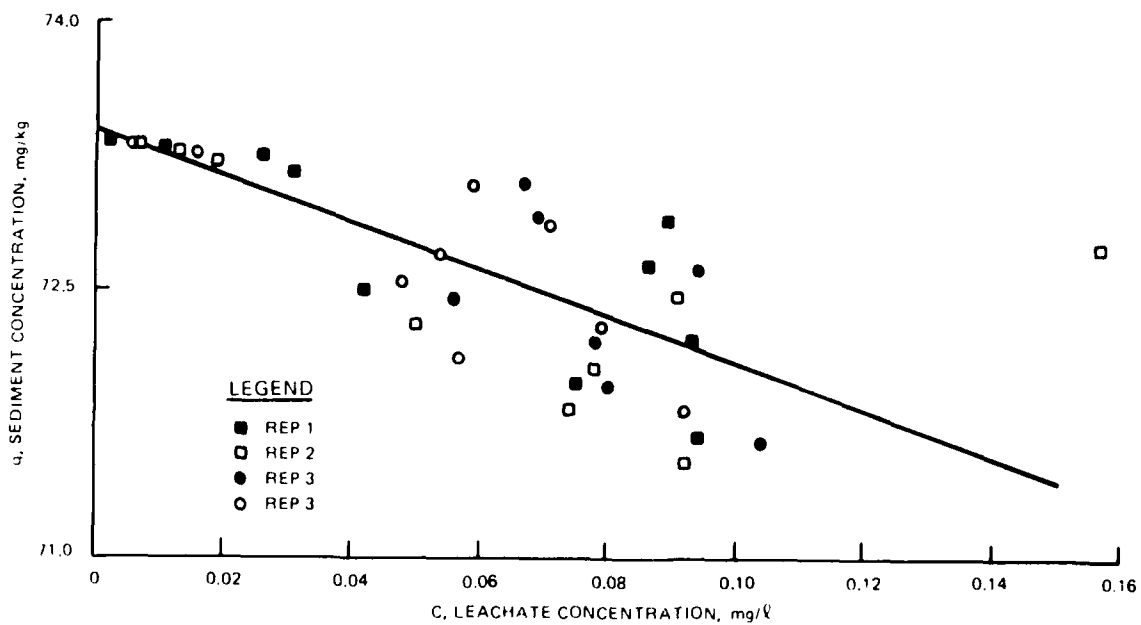


Figure A6. Copper desorption isotherm for anaerobic Everett Harbor sediment

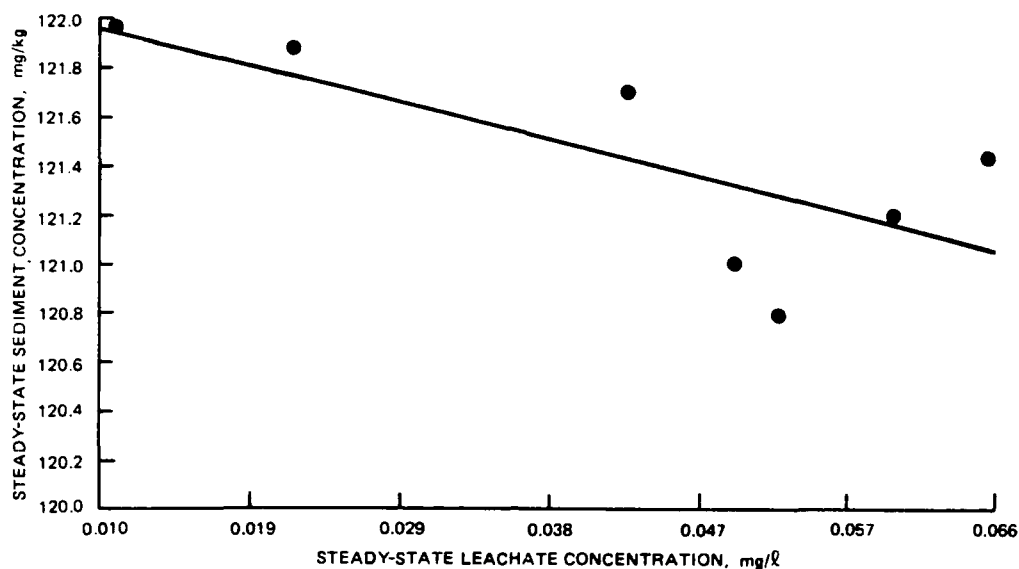


Figure A7. Desorption plot for nickel derived from sequential batch testing of anaerobic New Bedford Harbor sediment with distilled water

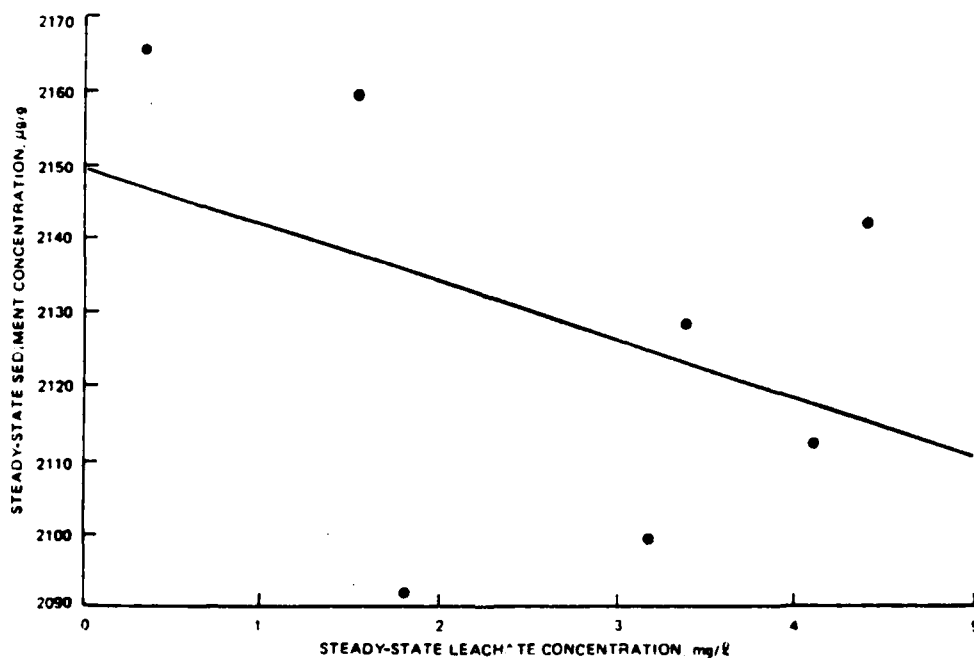


Figure A8. Total PCB desorption isotherm for New Bedford Harbor sediment distilled water sequential batch leach test

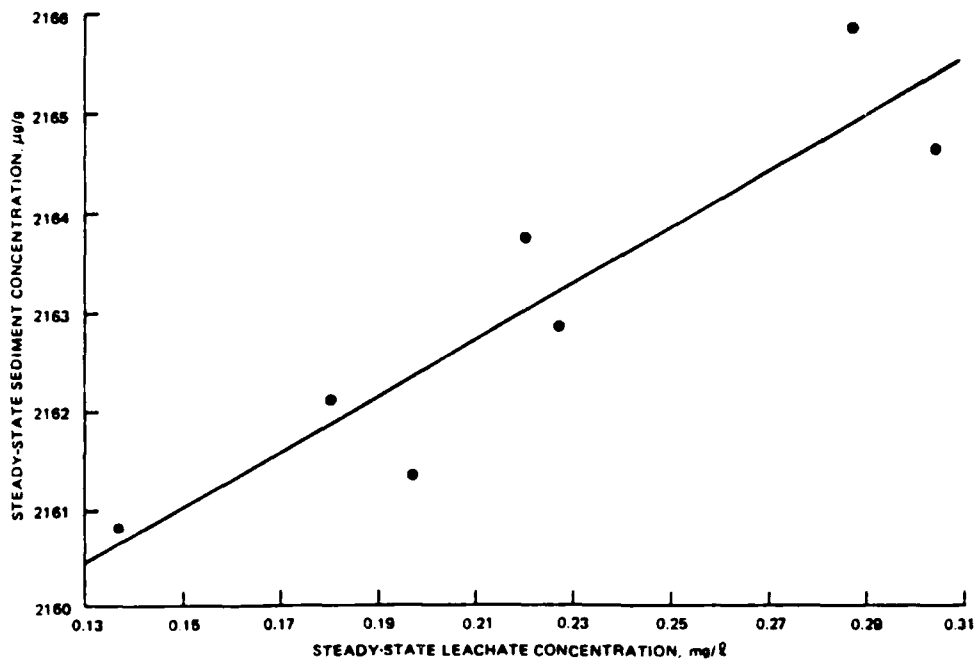


Figure A9. Total PCB desorption isotherm for New Bedford Harbor sediment saline water sequential batch leach test

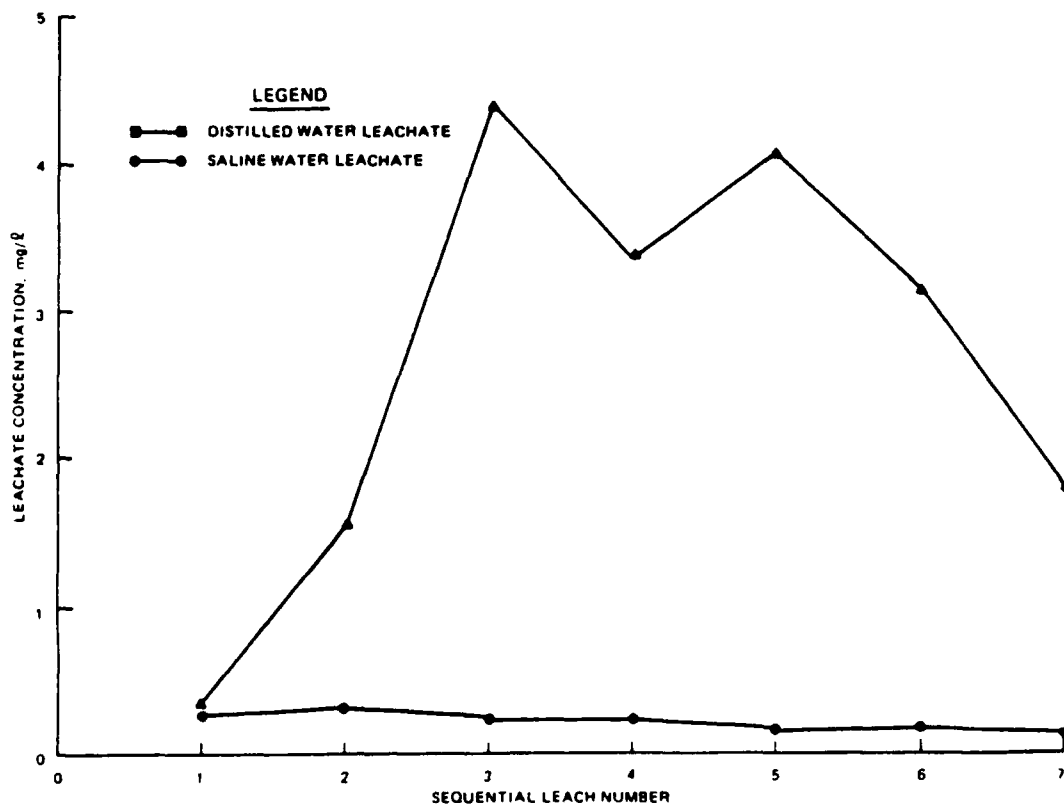


Figure A10. Total PCB concentrations in New Bedford Harbor sequential batch leachate

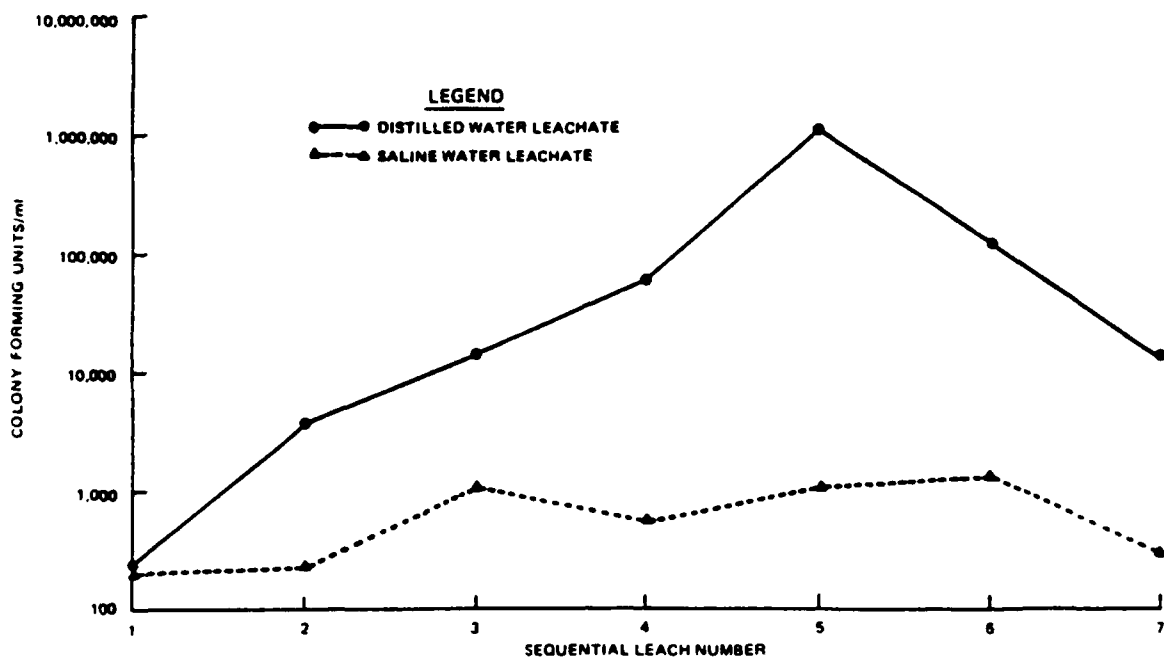


Figure A11. Microbe counts for New Bedford Harbor sequential batch leachate

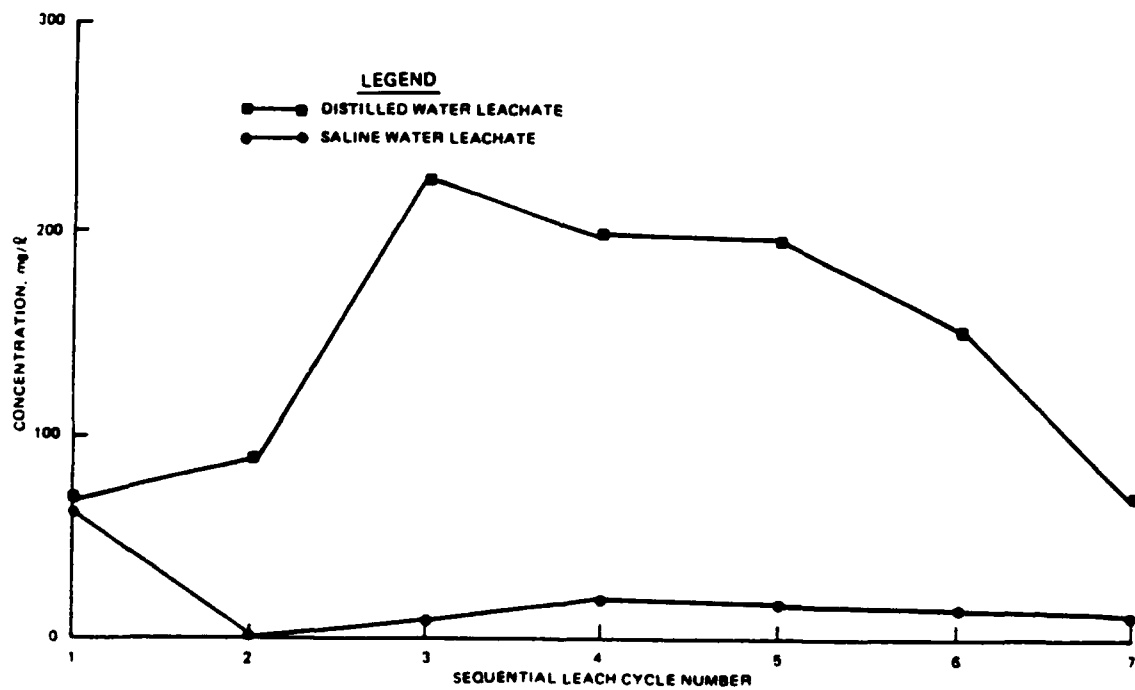


Figure A12. Dissolved organic carbon concentrations in New Bedford Harbor sequential batch leachate

APPENDIX B: SUMMARY OF RESEARCH METHODOLOGIES

Batch Tests

1. Batch tests were conducted to investigate the intrinsic contaminant release properties of the sediment under anaerobic and aerobic conditions. Batch testing procedures applied to the sediment included kinetic tests, liquid-solids ratio testing, sequential batch testing, and interstitial water extraction. These procedures are briefly described below. Further details of each procedure can be found in Environmental Laboratory (1987).*

Kinetic tests

2. Kinetic testing refers to a series of batch tests conducted to determine the shake time necessary to achieve steady-state soluble contaminant concentrations.

Liquid-solids ratio testing

3. Following determination of the shake time necessary to obtain steady-state concentrations in the leachate, testing to determine the proper liquid-solids ratio was conducted. Test procedures consisted of batch testing at varying liquid-solids ratios.

Sequential batch testing

4. Sequential batch leaching tests were applied to anaerobic and aerobic sediment following selection of a 4:1 liquid-solids ratio and a shaking time of 24 hr. General test procedures for metal and organic contaminants are detailed in Table B1.

Interstitial water extraction

5. Interstitial water samples for metal and organic contaminant analysis were obtained by centrifugation of the sediment. Polycarbonate centrifuge tubes were used for samples being tested for metals from anaerobic sediment. Stainless steel (450-ml) centrifuge tubes were used in the anaerobic sediment analysis for organic contaminants. Anaerobic testing for both organic and metal contaminants was performed under a nitrogen atmosphere.

* See References at the end of the main text.

Column Tests

6. Continuous-flow column leaching tests were conducted in divided-flow stainless steel permeameters designed to minimize wall effects and provide for pressurized operation (see Figure A2, Appendix A). The bottom ring divides flow, separating the leachate flowing through the center of the column from that flowing down the walls, thereby minimizing wall effects. The applied pressure (maximum of 25 psi (172 kPa) forced water through the sediment at rates sufficient to allow sample collection in a reasonable period.

Leachate Quality Prediction

7. A permeant-porous media equation was used to predict permeameter leachate quality as a function of volume throughput. The source term in the predictive equation for interphase transfer of contaminant from the dredged material solids to the leachate was modeled as equilibrium-controlled, linear desorption.

Integrated Approach

8. The integrated approach combines batch leach tests, column leach tests, and an equation to predict permeameter leachate quality as a function of volume throughput (time). The results of these tests and calculations are used to test the hypothesis that contaminant leaching from sediment can be described as equilibrium-controlled, linear desorption. Application of the integrated approach is illustrated in Figure A3 (Appendix A).

Table B1
Test Sequence for Sequential Batch Leaching

<u>Step</u>	<u>Procedure</u>
1	Load sediment into appropriate centrifuge tubes: 500-ml polycarbonate for metals and 450-ml stainless steel for organic contaminants. Add sufficient water to each tube to bring final water-to-sediment ratio to 4:1. Sufficient stainless steel tubes must be loaded to obtain enough leachate for analysis and for use in leaching fresh sediment.
2	Shake mixtures for 24 hr.
3	Centrifuge for 30 min at $6,500 \times g$ for organics and $9,000 \times g$ for metals.
4	Filter leachate through 0.45- μ m membrane filters for metals or through a Whatman GF/D glass fiber prefilter followed by passage through a Gelman AE glass fiber filter of 1.0- μ m nominal pore size.
5	Set aside a small amount of leachate for analysis of pH and conductivity; then, acidify leachate for organic analysis with HCl and leachate for metals analysis with Ultrex nitric acid. Store leachate for organic analysis in acetone-rinsed glass bottles and leachate for metals analysis in plastic bottles.

Note: The anaerobic integrity of the sample was maintained during sample addition to centrifuge tubes, shaking, centrifugation, and filtration.